

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 13, 1999	3. REPORT TYPE AND DATES COVERED Final		
4. TITLE AND SUBTITLE Molecular Engineering of Smart Polymer Surfaces		5. FUNDING NUMBERS DAAH04-95-1-0592		
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9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211		10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 34536.8-ms		
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.		12 b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) Two approaches for the development of smart functional polymer surfaces are described: surface-active end-functional block copolymers and monolayers with light-switchable surface properties. End-functional diblock copolymers of the type poly(styrene-b-dimethylsiloxane)-silane adsorb at the surface of a polystyrene matrix and deliver the silane group to the surface. When contacted with a polysiloxane gel, adhesion is promoted via an hydrosilylation reaction between the silane end group and residual vinyl functionality in the gel; when the surface is placed against poly(methyl methacrylate), release behavior is observed. Bonding to the latter substrate can be enhanced by replacing the silane functionality with a carboxylic acid. These modified substrates are the first examples of selective adhesives for polymeric materials. Theoretical and experimental studies of other model functional polymers have also been completed that establish an understanding of both the equilibrium and dynamic behavior of functional polymer surfaces. The second thrust of research concerns the assembly of azo-dye monomeric and polymeric monolayers that change molecular configuration and therefore surface properties when exposed to light. The two approaches under study constitute novel methods for the delivery of specific functional groups to polymer surfaces and impact a broad range of polymer technologies including adhesives, coatings, release and wetting.				
14. SUBJECT TERMS		15. NUMBER OF PAGES 5		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

(1) Manuscripts submitted or published during grant period

1. "Polymer Surfaces and Interfaces", J. T. Koberstein, MRS Bulletin, 21(1),16-17, (1996).
2. "Surface and Interface Modification of Polymers", J. T. Koberstein, MRS Bulletin, 21(1),19-23, (1996).
3. "Monolayer Dynamics of Functionally-Terminated Poly(dimethyl Siloxane) at the Air/Water Interface", F. E. Runge, H. U. Stauffer, T. J. Lenk, J. T. Koberstein and H. Yu, Langmuir, accepted.
4. "End Group Effects on Surface Properties of Polymers: Semi-Empirical Calculations and Comparison to Experimental Surface Tensions for α,ω -Functional Poly(dimethyl siloxanes)", Claire Jalbert, Jeffrey T. Koberstein, Arvind Hariharan and Sanat K. Kumar, Macromolecules 30(15),4481-4490 (1997).
5. "Creating Smart Polymer Surfaces with Selective Adhesion Properties", J. T. Koberstein, D. E. Duch, W. Hu, T. J. Lenk, R. Bhatia, H. R. Brown, J.-P. Lingelser, and Y. Gallot, J. Adhesion, 66, 229-249 (1998).
6. "Tailoring Polymer Interfacial Properties by End Group Modification", J. T. Koberstein, in "Polymer Surface, Interfaces and Thin Films", "Series on Directions in Condensed Matter Physics, World Scientific Publishing, in press.
7. "The Effects of Low Energy End Groups on the Dewetting Dynamics of Poly(styrene) Films on Poly(methyl methacrylate) Substrates", C. Yuan, M. Ouyang and J. T. Koberstein, Macromolecules, 32 (7), 2329-2333 (1999).
8. "Segregation Dynamics of Block Copolymers to an Immiscible Polymer Blend Interface", D. Cho, C. Jalbert and J. T. Koberstein, submitted to Macromolecules.
9. "The Effects of End Groups on Thermodynamics of Polymer Blends. III. LCST Phase Diagrams", P. A. Schacht and J. T. Koberstein, submitted to Macromolecules.

(2) Scientific Personnel Supported by this Project during this period:

Patricia O'Rourke (PhD candidate in Chemical Engineering)
Ralf Mason (PhD candidate in Polymer Science)
Young Jun Kim (postdoctoral associate)
Ciagen Yuan (postdoctoral associate)
D. Duch (received MS degree in Polymer Science, 1995)
E. Jerry Pickering (received PhD in Polymer Science, 1996)

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(3) Inventions

"Ultra thin silicon oxide and metal oxide films", U, S, Patent 5661092, granted 08/26/97.
Amendment A granted April 8, 1999

(4) Scientific Progress

Previous funding supported work that was concentrated in several areas: lubrication properties of thin polymer films^{1,2,3}, the surface properties of end-functional polymers, end-functional surface-active block copolymers as additives that promote selective adhesion, and light activated polymer surfaces. Our collective work on functional polymers was reviewed in a recent book chapter⁴.

End Group Effects on Surface Properties. - In collaboration with Dr. Sanat Kumar's research group, we developed a lattice theory⁵ to calculate both the surface tension and surface structure of end-functional homopolymers. The theoretical surface tension is calculated from the predicted surface composition, and surface tension contributions of end groups and backbone estimated by group contribution methods. In addition to reproducing the experimental surface tension behavior of α,ω -

functional poly(dimethyl siloxane), the theory yielded several important findings. Segregation of end groups was controlled almost entirely by enthalpic effects related to the difference in surface energy between the end group and backbone. Entropy was found to be virtually irrelevant in affecting the surface composition. When the surface tension difference between end group and backbone is negative, end groups are adsorbed at the surface. An end group depletion layer forms when the difference is positive. In both cases, the end group concentration gradient has two regions of behavior. The initial gradient is an adsorption or depletion zone that is only one lattice layer thick. The second region of the gradient covers a depth from the second lattice layer to the radius of gyration. If the first lattice layer is depleted, the second lattice layer exhibits an excess; if the first layer is in excess the second lattice layer shows depletion. The end group composition in the second region has its maximum magnitude in the second lattice layer and thereafter monotonically decays to the bulk value. This result has important implications for the behavior of all functional polymer surfaces. Although there may be a depletion layer of functional groups at a surface, it is always followed by an excess layer only about one nanometer below the surface. Reorganization of functionalized polymer surfaces is therefore expected to be relatively easy because a functional group need only move about one nanometer to relocate itself at the surface.

The nature of the surface end group gradients was probed by angle-dependent X-ray photoelectron spectroscopy (ADXPS) measurements on two systems: amine-terminated PDMS (published previously), where the high energy end groups are depleted from the surface, and fluorosilane-terminated poly(styrene) (PS) for which the end groups are attracted to the surface. These results document the expected end group adsorption⁶ and depletion⁷ behavior.

Ms. P. O'Rourke has just completed a tour de force calculation that extends the previous theoretical work on α,ω -end-functional polymers to include α -functional homopolymers, polymers with a single functional group at any location along the chain, adjacency effects (i.e., two functional groups together), and the use of a repulsive high energy group to aid in locating a low energy group at the surface (i.e., a "push me-pull you" effect). The results were presented at a recent meeting⁸ and the manuscript will be submitted for publication shortly.

Reorganization of Polymer Surfaces. - The reorganization of surfaces of end-functional polymers was investigated for poly(styrene) terminated with fluorosilane and carboxylic acid end groups. This experiment effects an abrupt change in the surface interaction parameter, whereupon the surface composition attempts to readjust to the new equilibrium. The results for the fluorosilane-terminated PS show that the surface in air is initially enriched in the end group, but under hydrophilic conditions reorganizes until the surface is essentially pure poly(styrene). The surface of the carboxy-terminated PS is essentially pure poly(styrene) initially, and reorganizes to relocate carboxylic acid groups at the surface. ADXPS measurements on the fluorosilane-terminated poly(styrene) demonstrate that, after exposure to water vapor, the deep portion (i.e., about 3-7nm below the surface) of the end group concentration gradient is unchanged, and that surface fluorosilane end groups relocate about 1-2nm below the surface. This data reinforces the result from the lattice theory that the composition of only the top nanometer of a material controls the surface energy. The kinetics of surface reorganization were found to follow an Arrhenius dependence on temperature, suggesting that short range Rouse-like motions were sufficient to reorganize the surface of even a glassy polymer. This important result demonstrates how surfaces can rearrange well below the glass transition temperature. These results were presented at a recent meeting⁹ and will be submitted for publication shortly.

End Group Effects on Wetting. - The end-fluorinated poly(styrene) was also found to be an effective macromolecular surfactant as an additive to a poly(styrene) matrix. The additives show a strong adsorption isotherm and yield surfaces that can be highly enriched in the fluorinated end group. In recent work, it was demonstrated that these additives can be employed successfully to control the dewetting transition of poly(styrene) thin films on poly(methyl methacrylate) substrates, as well as control the rate of hole growth in dewetting films¹⁰.

End Group Effects on Bulk Thermodynamics. End groups substitution was shown to decrease the upper critical solution temperature for blends of poly(isoprene) and α,ω -functional poly(dimethyl siloxane)¹¹ by as much as 150C. This behavior was successfully explained in terms of binary interaction theory treating the end-functional homopolymer as if it were a random copolymer of end group and backbone units. A similar theoretical framework was successful in explaining the effects of end group substitution on the lower critical solution temperature of a blend of poly(styrene) with poly(vinyl methyl

ether)¹². We now have a means to describe how end groups affect the bulk thermodynamics of binary homopolymer blends exhibiting both upper and lower critical solution temperatures.

End-Functional Block Copolymers. We have investigated the segregation kinetics¹³ of surface-active ω -functional block copolymers and found that they offer a convenient approach for surface delivery of a high energy end group to a surface to which it would not normally go to. These copolymers consist of an anchor block of the matrix homopolymer, and a surface-active block terminated with a functional group. When added to a homopolymer matrix, the block copolymer spontaneously self-assembles at the surface, thereby delivering the functional end group to the vicinity of the air-polymer interface. The adsorption isotherm is independent of the end group type. Poly(styrene) modified with ω -functional poly(styrene-*b*-dimethylsiloxane) diblock copolymers was found to exhibit selective adhesion toward crosslinked poly(dimethylsiloxane) and poly(methyl methacrylate) (PMMA) substrates¹. The strength of the PS-PDMS interface was improved¹⁴ by the addition of a silane terminated copolymer due to a reaction with residual vinyl functionality in the PDMS gel. The same copolymer reduced the adhesion between a PS matrix and a PMMA substrate¹, since no such reaction can occur. The adhesion between PS and PMMA was enhanced, however, with a carboxylic acid terminated copolymer due to an acid-base interaction between PMMA and the carboxylic acid end group. This work represents the first example of selective adhesive properties for a polymeric substrate. It is remarkable that the adhesion depends only on the chemical nature of the terminal group on the polymer chain.

Light Activated Polymer Surfaces. - The work on light switchable surfaces has focused on amassing a number of azo-dye labeled samples to study. We have formed a collaboration with Dr. Prescher from Berlin to obtain azo dyes and side chain azo polymers containing perfluoro end groups on the azo moieties. When light is applied, the perfluoro groups are switched up and down to the surface. We have prepared some Langmuir Blodgett films of these materials and are beginning to test their surface properties. We have also created a collaboration with Prof. Juergen Ruehe and Prof. Wolfgang Knoll at the Max-Planck Institute in Mainz Germany to synthesize some new azo-side chain polymers specifically for these studies. The PhD student on this project, Ms. O'Rourke recently spend two months in Germany, funded by a NATO grant to make the new materials, and a German student spent two months in our laboratories. Due to a badly broken leg, Ms. O'Rourke was forced to curtail some of the laboratory work in this area and therefore concentrated on the aforementioned theoretical work.

(5) Technology Transfer

Dr. Koberstein continues to pursue collaborative work with Dow Corning, Wentworth Laboratories and International Paper company to pursue development of our patent on silicon oxide films. This technology is also part of a grant to develop new coating technologies for the Air Force Office of Scientific Research. Finally, we are discussing the technology on functional block copolymers with a company as a means of delivering antimicrobial agents to the surface of polymers.

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- 2 "Boundary Lubricating Properties of Ultrathin Films of Functionally-Terminated Oligomers", C. L. Mirley and J. T. Koberstein, submitted to *Langmuir*.
- 3 "Boundary Lubrication and Wear Properties of Silicon Oxide and Metal Oxide Films Prepared by a UV/Ozone Conversion Method", C. L. Mirley and J. T. Koberstein, submitted to *Langmuir*.
- 4 "Tailoring Polymer Interfacial Properties by End Group Modification", J. T. Koberstein, in "Polymer Surface, Interfaces and Thin Films", "Series on Directions in Condensed Matter Physics, World Scientific Publishing, in press.
- 5 "Monolayer Dynamics of Functionally Terminated Poly(dimethyl siloxanes) at the Air/Water Interface" F. Runge, H. Stauffer, T. Lenk, J. Koberstein, H. Yu, *Langmuir*.
- 6 "Surface Segregation in End-Fluorinated Polystyrenes", R. Mason, C. Jalbert, J. Elman, T. Long, B. Gunesin, and J. T. Koberstein, *Polymer Preprints, American Chemical Society*, 39(2), 910, 1998, Boston, MA, August 25, 1998..

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- 7 "Distribution of End Groups at the Surface of End-Functional Poly(dimethyl siloxane)", R. Mason, C. Jalbert and J. T. Koberstein, in preparation for submission to *Macromolecules*.
 - 8 "Surface Properties of End and Center-Functional Polymers, with P. O'Rourke, *Amer. Chem. Soc., PMSE preprints*, 78, 205, 1998, Dallas, April, 1998.
 - 9 "Surface Reorganization Kinetics of a Model End-Functionalized Polymer System", D. Wong, C. Jalbert, and J. T. Koberstein, *Polymer Preprints, American Chemical Society*, 39(2), 901, 1998, Boston, MA, August 25, 1998.
 - 10 "The Effects of Low Energy End Groups on the Dewetting Dynamics of Poly(styrene) Films on Poly(methyl methacrylate) Substrates", C. Yuan, M. Ouyang and J. T. Koberstein, *Macromolecules*, 32 (7), 2329-2333 (1999).
 - 11 "The Effect of End Groups on Thermodynamics of Immiscible Polymer Blends: II. UCST Phase Diagrams", M. Lee, C.A. Fleischer, A. R. Morales, R. Konigsveld and J. T. Koberstein, in preparation for submission to *J. Polym. Sci. Polym. Phys. Ed.*
 - 12 "The Effect of End Groups on Thermodynamics of Immiscible Polymer Blends: III. LCST Phase Diagrams", with C.A. Fleischer, and A. R. Morales, submitted to *Macromolecules*.
 - 13 "Segregation Kinetics of Diblock Copolymers to Air-Polymer and Polymer-Polymer Interfaces", D. Cho, W. Hu, and J. T. Koberstein, submitted *Macromolecules*.
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